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Structure and surface morphology of $LiCoO_2$ thin film cathodes prepared by pulsed laser deposition

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Thin films of $LiCoO_2$ were grown by pulsed laser deposition technique on silicon substrates. Structural and microstructural properties were studied. The XRD pattern for the $LiCoO_2$ film deposited at substrate temperature of 600 ^{0}C in pO_2 = 200 mTorr revealed that the film had few low intensity (1 0 1), (0 0 6), (0 1 2), (1 0 4), (0 1 8) and (1 1 0) peaks with predominating (0 0 3) peak. The XRD pattern of $LiCoO_2$ thin films deposited at substrate temperature of 600 ^{0}C in pO_2 = 300 mTorr showed characteristic peaks i.e. (0 0 3), (1 0 1), (0 0 6), (0 1 2), (1 0 4), (0 1 8) and (1 1 0) have been increased with oxygen pressure. The appearance of predominating (003) peak indicates that the growth of crystallites is parallel to c-axis. The atomic force microscopy (AFM) data demonstrated that the deposited $LiCoO_2$ thin films are homogeneous. The morphological pattern of the deposited film at substrate temperature of 600 ^{0}C in pO_2 = 200 mTorr demonstrated that the film contains uniformly distributed irregular shaped grains. Though the particle sizes are seems to be small, the presences of coagulated particles are appeared in the AFM image. The morphological changes were noticed to be predominant at higher oxygen pressures and the changes are associated with the grain size and their shape distribution.

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1. Introduction

Advances in science and engineering related to the emerging technologies of lithium-ion batteries (LIBs) have been so spectacular in the past decade that they have become the most popular power source for portable computing, battery cars, microelectronics, biomedical implantable devices and telecommunication [1, 2]. There is a growing interest in thin film batteries with smaller dimension. The cathode is one of the critical components of a lithium-ion battery and it determines the capacity, cyclic performance and thermal stability of the battery. In order to improve the electrochemical properties of the cathode material, researchers have attempted to modify the cathode surface by using stable materials [3, 4]. The layered transition metal oxide compounds which are composed of hexagonal close packed oxygen atoms network with lithium and transition metal ions in an alternating (111) planes, such as $LiCoO_2$, $LiNiO_2$, $LiCo_xNi_{1-x}O_2$ etc. have been studied extensively as alternate cathode materials for low power applications. Among them, $LiCoO_2$ has found large scale potential applications in the commercial lithium ion batteries. Although intensive investigations have been devoted in finding most cost effective and less toxic alternate materials like $LiMnO_2$, $LiMn_2O_4$ etc., $LiCoO_2$ is still so far the most successful, and reliable choice due to superior cycling stability and power density. Also it has been widely used as cathode material due to advantages of high specific capacity, high operating voltage, good reversibility, low self-discharge and long cycle life. For the cathode materials, $LiCoO_2$ is extensively studied and applied. The reason for this success is that Li^+ ions can be deintercalated from $LiCoO_2$ down to $Li_{0.5}CoO_2$ with a very good reversibility and a high electrochemical potential, giving rise to batteries with a good cyclability and a high voltage [5].

The structure of layered $LiCoO_2$ has Rhombohedral symmetry and belongs to the space group R3m, and is ideally suited to accommodate large changes in Li concentration. This crystal structure consists of close-packed oxygen ion layers separated by alternating layers of Li and Co ions [6]. Electrochemical performance of $LiCoO_2$ greatly depends on its crystallographic structure, as it exists in two different modifications: a high temperature phase of $LiCoO_2$ (HT- $LiCoO_2$) with a-$NaFeO_2$ structure (R3m) and a low temperature phase of $LiCoO_2$ (LT- $LiCoO_2$) with a spinel-like structure (space group Fd3m) [7]. Usually, the HT- $LiCoO_2$ phase demonstrates a capacity about 0.5 V higher than the LT-$LiCoO_2$ phase in lithium batteries [8]. HT- $LiCoO_2$ has a layered-type (Rhombohedral) structure with symmetry R3m. The lithium and metal ions occupy alternate layers in octahedral sites between the cubic close-packed oxygen planes [9].

The structure and degree of cation ordering in $LiCoO_2$ vary with the synthetic conditions that affect its electrochemical activity. Recently, a number of new approaches for the preparation of $LiCoO_2$ with improved properties have been developed. $LiCoO_2$ thin films can be obtained by various techniques such as radio frequency (rf) sputtering [10, 11], pulsed laser deposition (PLD) [12-17], electrostatic spray deposition [18] and chemical vapour deposition [19]. Many efforts have been devoted to investigate the crystal structure and electrochemical properties of $LiCoO_2$. Even though the technology is rather expensive and the material is highly toxic, lithium cobaltate is still the most widely used cathode material in lithium-ion batteries.

PLD has been widely recognized as a very promising, versatile and efficient method for the deposition of metal oxide thin films [20]. PLD is a powerful and flexible technique for fabricating simple and complex metal oxide films, and has several advantages for thin film deposition: (1). Direct stoichiometry transfer from the target to the growing film. (2). High deposition rate and inherent simplicity for the growth of multilayered structures. (3). Dense, textured films can be produced more easily by PLD with in situ substrate heating. Iriyama et al. [15] prepared thin films of $LiCoO_2$ by PLD and studied the electrochemical performance. In thin film deposition, the oxygen partial pressure plays the important role of determining the microstructure and surface morphology of films. In this study, we have deposited $LiCoO_2$ thin films on silicon substrates and investigated the structural properties of thin film cathodes.

2. Experimental

$LiCoO_2$ films were grown by pulsed laser deposition technique. $LiCoO_2$ target was prepared by sintering a mixture of high purity $LiCoO_2$ and Li_2O powders (Cerac products) with excess of Li i.e. Li/Co > 1.0 by adding Li_2O. The mixture was crushed and pressed at 5 tonns.cm^{-2} to make tablets of 3 mm thick and 13 mm diameter. To get quite robust targets, the tablets were sintered in air at 800 ^{0}C. The typical substrates i.e. Si wafers were cleaned using HF solution. The target was rotated at 10 rotations per minute with an electric motor to avoid depletion of material at any given spot. The laser used in these experiments is the 248 nm line of a KrF excimer laser (Luminics PM 882) with 10 ns pulse with a repetition rate of 10 Hz. The rectangular spot size of the laser pulse was 1x3 mm^2 and the energy 300 mJ. The target substrate distance was 4 cm. The deposition temperature was maintained with thermocouple and temperature controller. During the deposition pure oxygen was introduced into the deposition chamber and desired pressure was maintained with a flow controller [21, 22]. The structure of the films was characterized by X-ray diffraction using a diffractometer (Philips model PW 1830) with nickel filtered CuK_α radiation (l= 1.5406 A^0). The diffraction pattern were taken at room temperature in the range $10^0 < 2\theta < 80^0$ using step scans. The surface topography was investigated by atomic force microscopy (AFM) using a bench apparatus (Digital instruments, 3100 series).

3. Results and discussion

Pulsed laser deposited $LiCoO_2$ films are pin-hole free as revealed from optical microscopy and well adherent to the substrate surface. The thickness of $LiCoO_2$ films is 250 nm. The structure and surface morphology of the films are studied.

3.1 Structure

The XRD patterns were recorded in the diffraction angle (2θ) range 10^0 to 80^0 with a scan rate of 1^0/min. The XRD pattern for the $LiCoO_2$ film deposited at substrate temperature of 600 ^{0}C in pO_2 = 200 mTorr is shown Fig. 1. The XRD data revealed that the film had few low intensity (1 0 1), (0 0 6), (0 1 2), (1 0 4), (0 1 8) and (1 1 0) peaks with predominating (0 0 3) peak at their relative 2θ positions. The observed X-ray reflecting Bragg angle positions of $LiCoO_2$, corresponding prominent peaks and the inter-planar distances (d) result that the deposited $LiCoO_2$ thin films having hexagonal structure. The calculated lattice parameters from the XRD spectra were slightly deviated to the values reported from the literature. This may be due to lower crystallite size which leads to the development of internal strain in the lattice [23]. To enhance the crystallinity, homogeneity and to have the reduction in the internal lattice strains the oxygen pressure was varied. The XRD pattern of $LiCoO_2$ thin films deposited at substrate temperature of 600 ^{0}C in pO_2 = 300 mTorr is shown in Fig. 2. From the XRD results, it is observed that the intensity of the characteristic peaks i.e. (0 0 3), (1 0 1), (0 0 6), (0 1 2), (1 0 4), (0 1 8) and (1 1 0) have been increased with oxygen pressure. The appearance of predominating (003) peak indicates that the growth of crystallites is parallel to c-axis. This is due to rearrangement of the atoms which leads to the formation of large homogeneous grains with polycrystalline nature. Generally, $LiCoO_2$ host intercalation matrix is regarded to be derived from the NaCl structure. The structure is rhombohedral in shape (space group *R3m*) with atoms in the following positions: Cobalt 'Co' atoms in '3a' sites (0 0 0), Lithium 'Li' atoms in '3b' sites (0 0 ½) and Oxygen 'O_2' atoms in '6c' sites ± (0 0 z) with z ≈ 0.25. Cobalt and Lithium alternatively occupy octahedral sites (1 1 1) between adjacent close packed planes of oxygen.

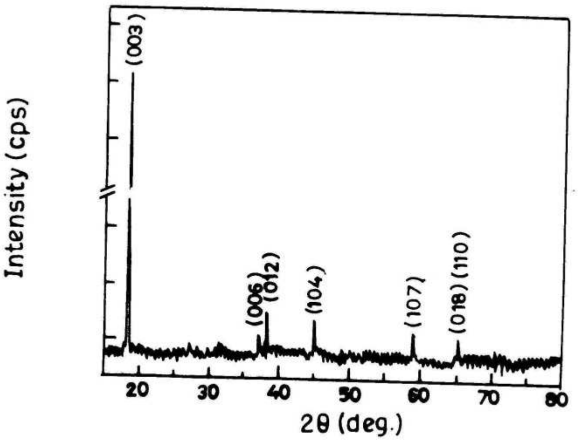

Fig. 1. XRD pattern of $LiCoO_2$ thin film deposited at substrate temperature of 600 ^{0}C in pO_2 = 200 mTorr.

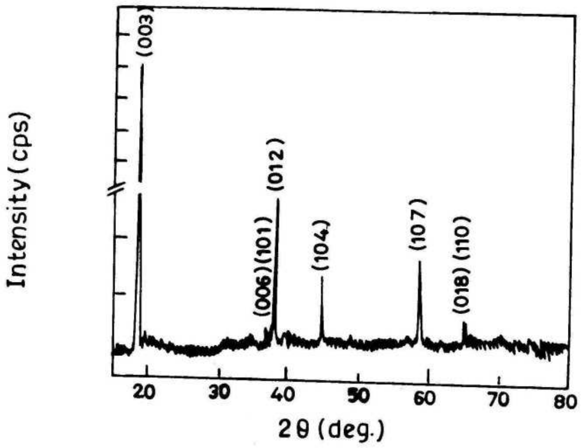

Fig. 2. XRD pattern of $LiCoO_2$ thin film deposited at substrate temperature of 600 ^{0}C in pO_2 = 300 mTorr

3.2 Surface morphology

The surface morphology of the films has been performed using Atomic force microscopy. Fig. 3 shows the morphological pattern of the deposited film at substrate temperature of 600 ^{0}C in pO_2 = 200 mTorr. The data demonstrates that the film is homogeneous and uniformly distributed irregular shaped grains. The morphological image illustrates that the films are seems to be porous. Though the particle sizes are seems to be small, the presences of coagulated particles are appeared in the AFM image. The particle formation is in aggregated form with roughly spherical in shape. Fig. 4 shows the morphological image of the deposited film at substrate temperature of 600 ^{0}C in pO_2 = 300 mTorr. The morphological changes were noticed to be predominant at higher oxygen pressures and the changes are associated with the grain size and their shape distribution [24]. From the AFM data, it is observed that these films are also in porous in the aggregated form, but the average particle size is increased. The increase in the area fraction may be due to the increased compound aggregation by the influence of the higher oxygen pressure.

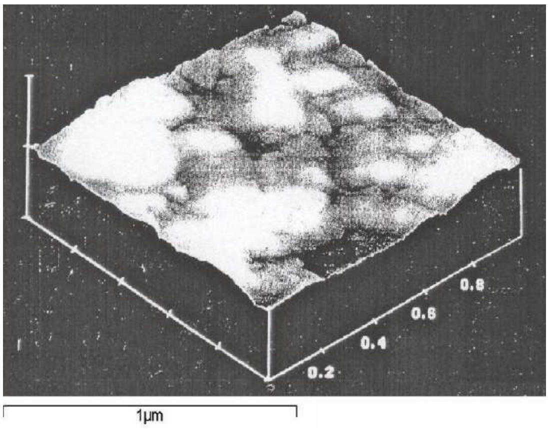

Fig. 3. AFM image of $LiCoO_2$ thin film deposited at substrate temperature of 600 ^{0}C in pO_2 = 200 mTorr

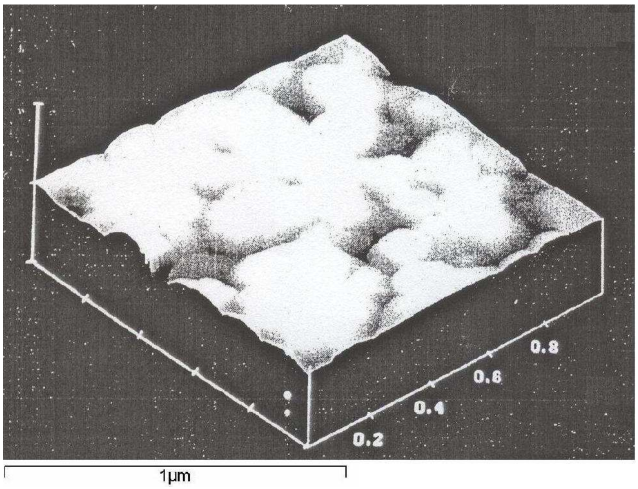

Fig. 4. AFM image of $LiCoO_2$ thin film deposited at substrate temperature of 600 ^{0}C in pO_2 = 300 mTorr

4. Conclusion

Thin films of $LiCoO_2$ were grown by pulsed laser deposition technique. Structural and microstructural properties were studied. The XRD pattern for the $LiCoO_2$ film deposited at substrate temperature of 600 ^{0}C in pO_2 = 200 mTorr revealed that the film had few low intensity (1 0 1), (0 0 6), (0 1 2), (1 0 4), (0 1 8) and (1 1 0) peaks with predominating (0 0 3) peak where as the film deposited at substrate temperature of 600 ^{0}C in pO_2 = 300 mTorr showed characteristic peaks i.e. (0 0 3), (1 0 1), (0 0 6), (0 1 2), (1 0 4), (0 1 8) and (1 1 0) have been increased with oxygen pressure. The appearance of predominating (003) peak indicates that the growth of crystallites is parallel to c-axis. The morphological changes were noticed to be predominant at higher oxygen pressures and the changes are associated with the grain size and their shape distribution.

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